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European Patent Office  
Office européen des brevets



(11)

**EP 0 887 199 A2**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**30.12.1998 Bulletin 1998/53**

(51) Int. Cl.<sup>6</sup>: **B41M 5/00**

(21) Application number: **98111534.8**

(22) Date of filing: **23.06.1998**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

Designated Extension States:

**AL LT LV MK RO SI**

(30) Priority: **26.06.1997 JP 170168/97**

**26.06.1997 JP 170169/97**

**26.06.1997 JP 170170/97**

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**(54) Ink jet recording sheet**

(57) The present invention provides an ink jet recording sheet which is excellent in image sharpness, has no waviness even after image recording and drying, has no nonuniformity of coating of the ink-receiving layer surface, and is excellent in quality of image, when the sheet is used in an ink jet recording method using aqueous ink. This object has been achieved by an ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, wherein the ink-receiving layer is formed on the substrate having a density of 1.01 g/cm<sup>3</sup> or more, a Cobb sizing degree of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup>, an unevenness in thickness in machine direction (Rpy) of 150 mV or less and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6 µm or less as measured with a tracer type three-dimensional surface roughness meter.

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## Description

## BACKGROUND OF THE INVENTION

5 The present invention relates to an ink jet recording sheet, more particularly an ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer formed on the substrate, which permits formation of images of high quality by an ink jet recording method using aqueous ink, has slight waviness after recording, and has excellent characteristics.

10 The ink jet recording method performs recording of letters or images by allowing ink droplets ejected by various working principles to deposit on a recording sheet such as paper. The ink jet recording has such favorable features that it makes high-speed recording possible, that it produces little noise, that it can easily perform multi-color recording, that there is no limitation as to kind of patterns, and that it requires no developing-fixing. Thus, the ink jet recording is rapidly becoming widespread as devices for recording various characters including kanji and color images. Furthermore, the images formed by the multi-color ink jet recording method are by no means inferior to those printed by a multi-color press or those obtained by a color-photography. Besides, use of the ink jet recording extends to a field of full-color image recording where the number of copies is not so large, since it entails less costs per copy than employment of the photographic process.

15 In order that woodfree papers or coated papers for ordinary printing or writing can be used as the recording sheets for ink jet recording, efforts have been made to improve printer hardwares or ink composition. However, improvements in the recording sheets have come to be required increasingly in order to go side by side with developments in printer hardwares, such as ever increasing speed, development of ever finer definition and images of full color. That is, the recording sheets are required to have the following properties: the image density of printed ink dots is high and their hue characteristics are bright and appealing; the ink absorbing speed is so high that the ink applied does not bleed or spread even if the recorded dots are put over additionally; the diffusion of the recorded dots in the plane direction is not greater than needed and the circumference of dots is sharp and demarcating; and the quality of images is not changed with time or by circumstances, for example, the recording sheets are excellent in light resistance, water resistance, ozone resistance, etc.

20 For satisfying these requirements, several proposals have been put forward. For improving the ink absorption and preventing the diffusion of the recorded dots, there have been proposed, for example, methods comprising formation of an ink-receiving layer on a support (Japanese Patent Kokai Nos. 52-9074 and 58-72495, etc.) and a method using a specific agent capable of adsorbing a dye component, as a result of paying attention to the fact that the distribution of the dye component of ink in an ink-receiving layer affects the hue characteristics and sharpness of images (Japanese Patent Kokai No. 55-144172). For improving the light resistance, water resistance, ozone resistance, etc., there have been disclosed incorporation of a basic oligomer (Japanese Patent Kokai No. 60-11389), employment of a polyvinylamine copolymer in a base or a coat layer on the base (Japanese Patent Kokai No. 64-8085), etc. The requirements as to such characteristics, however, are becoming more difficult and severer.

25 On the other hand, ink jet printers have become inexpensive and have come to permit easy formation of images excellent in image reproducibility and color reproducibility, for example, sharpness and hue characteristics even by means of a personal computer. Accordingly, the ink jet printers have changed to generally used recording devices from special recording devices used by special persons. Since they can give images equal in quality to those of printed matters and photographs, they have come to be used also as printers for personally produced picture postcards or digital photographs. In this case, the same texture and feel as those of the picture postcards or photographic prints have come to be required. Moreover, when the ink jet printers are used for such a purpose, a large amount of ink is used, resulting in causing the following problem: a recording sheet after the recording has waviness due to a solvent contained in the ink which has reached the base paper of the sheet, so that the resulting print is not attractive. Therefore, the assurance of the characteristics described above is a requisite of an ink jet printer and an ink jet recording sheet.

30 With diversification of uses of ink jet recording sheets, they have come to be used as posters or POP arts. In addition, they have come to be used also as labels such as labels for price marking, labels for commodity indication (bar codes), labels for quality indication, labels for weight indication, labels (stickers) for advertisement, etc. by forming an adhesive layer on the reverse side of the sheet. Furthermore, since these ink jet recording labels adhere sufficiently to various adherends and hence are easy to attach, they can be attached to, for example, sheets with heat-sensitive properties, magnetic properties and offset printability through an adhesive layer to impart combined functions thereto. Therefore, their employment in railroad tickets, commutation tickets, various cards, etc. is becoming widespread.

35 Inks are classified into solvent-based inks and aqueous inks. The aqueous inks are more than the solvent-based inks because of their price, safety, ease of handling, etc. However, owing to the above-mentioned diversification of uses of ink jet recording sheets, the aqueous inks involve important problems such as the prevention of bleeding of the ink caused by the contact of water to a printed surface, and the reduction of waviness of the sheet caused by water which has reached the base paper. No sufficient measure to counter these problems, however, is taken, and the problems are

especially important and have to be promptly solved in ink jet recording sheets obtained by using as their medium a support composed mainly of natural pulp having a function as an ink absorber.

Ink jet recording sheets can be roughly classified according to their form into those of plain paper type represented by so-called fine papers • bond papers and those of coated type which comprise a support such as paper (e.g. fine paper), synthetic paper or synthetic resin film and an ink-receiving layer provided on the support. In the case of the ink jet recording sheets of coated type, various characteristics of the ink-receiving layer formed by coating directly affect the printing quality. Accordingly, there have been investigated the specific surface area and particle shape of pigments in view of absorption capacity; the transparency and refractive index of pigments in view of hue characteristics and color reproducibility; and coating layer structure, surface profile, etc. in view of quality of image. In addition, for reducing the waviness of the sheets after printing, there have been investigated the underwater elongation of the sheets as disclosed in Japanese Patent Kokai Nos. 3-38376, 3-133687, 3-199081 and 8-300809, their incorporation with synthetic fiber or glass fiber, a coating method, etc.

## SUMMARY OF THE INVENTION

The present invention is intended to provide an ink jet recording sheet which can give high-quality ink jet images excellent in hue characteristics and sharpness and is attractive with slight waviness after image recording when the sheet is used in an ink jet recording method using aqueous ink. The present invention is also intended to provide an ink jet recording sheet which is excellent in the coating properties of a coating solution for the ink-receiving layer, is free from nonuniformity of coating of the ink-receiving layer, and has a warm feel like paper.

In order to attain the above-mentioned performance characteristics, i.e., good printing quality and reduced waviness of a recording sheet after image recording, the present inventors earnestly investigated and consequently succeeded in preventing the waviness of an ink jet recording sheet after image recording by forming an ink-receiving layer on a paper substrate having a density higher than that of ordinary coated base paper or fine paper. In addition, the present inventors found that an ink jet recording sheet which is excellent in image sharpness and free from waviness after recording can be obtained by forming an ink-receiving layer on a paper substrate having a water absorption in a specific range. Since various characteristics of the formed ink-receiving layer largely depend on the paper substrate, the present inventors considered that the improvement of smoothness of the paper substrate is the most preferable means for obtaining a uniform ink-receiving layer. Thus, the present inventors have invented an ink jet recording sheet which is excellent in the coating properties of a coating solution for its ink-receiving layer, is free from nonuniformity of coating of the ink-receiving layer, is excellent in image sharpness, gives high-quality ink jet images, and has a warm feel like paper.

That is, the first aspect of the present invention is directed to an ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, wherein the ink-receiving layer is formed on the substrate having a density of sheet of 1.01 g/cm<sup>3</sup> or more as measured by the method prescribed in JIS P8118. The second aspect of the present invention is directed to an ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, wherein the ink-receiving layer is formed on the substrate having a Cobb sizing degree of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup> as measured by the water absorption test by Cobb sizing degree method prescribed in JIS P8140. Furthermore, the third aspect of the present invention is directed to an ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, wherein the substrate has an unevenness in thickness in machine direction specified hereinafter (Rpy) (hereinafter referred to as unevenness index) of 150 mV or less and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6 μm or less as measured with a tracer type three-dimensional surface roughness meter.

## DETAILED DESCRIPTION OF THE INVENTION

The ink jet recording sheets of the present invention are explained below in detail.

The ink jet recording sheet according to the first aspect of the invention comprises a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, said paper having a density of sheet of 1.01 g/cm<sup>3</sup> or more as measured by the method prescribed in JIS P8118.

The substrate used in the first aspect of the invention has a density of sheet of 1.01 g/cm<sup>3</sup> or more, preferably 1.03 g/cm<sup>3</sup> or more, more preferably 1.05 g/cm<sup>3</sup> or more. Investigation by the present inventors made it clear that specifically, the substrate having a density of sheet of 1.01 g/cm<sup>3</sup> or more can be obtained by adopting any of, preferably a combination of two or more of, the following methods (1) to (6).

(1) As the natural pulp used, hardwood pulp composed of short fibers and suited for producing paper with smooth

surface is used in a higher proportion. Specifically, for example, the hardwood pulp described or exemplified in Japanese Patent Kokai No. 60-69649 is used in a proportion of 60% by weight or more, preferably 75% by weight or more, based on the weight of a pulp mixture to be used.

(2) As to pulp beating conditions, pulp is beaten with a beater so that the content of long fibers may be as low as possible. The term "beating" referred to in the present specification denotes mechanical treatments to pulp wherein pulp slurry is passed through a relatively narrow clearance between a rotating rotor and a stationary stator. For example, "beating" includes a method wherein pulp slurry is treated in a batch system by use of a Hollander beater ordinarily used, and a refining treatment wherein a pulp slurry is passed through one refiner, or alternatively, several refiners which are arranged in series or parallel. Specifically, the pulp is beaten so that the weighted average fiber length may be 0.40 mm to 0.85 mm, preferably 0.45 mm to 0.75 mm, more preferably 0.45 mm to 0.70 mm, as measured according to JAPAN TAPPI Paper Pulp Testing Method No. 52-89 "Fiber Length Testing Method for Paper and Pulp", that the cumulative weight of fibers with a length of 1 mm or less may be 70% or more, and that the freeness of the beaten pulp may be 200 to 330 mlCSF.

(3) The substrate is made with a Fourdrinier machine so as to have a uniform formation, by applying a suitable paper making method to a pulp slurry containing additives. Specifically, for example, ① a proper turbulence is given to the pulp slurry, ② there is used a Fourdrinier machine having a suitable upper dewatering mechanism such as that described or exemplified in Japanese Patent Kokai No. 61-284762, and ③ as pressing in the wet part, multiplaten wet pressing, preferably three-platen or higher-order multiplaten wet pressing is carried out, and a smoothing roll is provided in the final platen of the pressing part.

(4) Wet re-press is employed in the course of drying wet paper. The term "wet re-press" referred to in the present specification denotes an apparatus which is provided in a drier zone and presses wet papers in a half dried state. For example, "wet re-press" includes a breaker stack. Specifically, the wet paper is subjected to multiplaten wet re-press such as that described or exemplified in Japanese Patent Kokai No. 3-29945.

(5) Any of various water-soluble polymers, hydrophilic colloids or polymer latices may be incorporated into or applied on the substrate. Specifically, any of various water-soluble polymers, hydrophilic colloids or polymer latices may be incorporated into or applied on the substrate in an amount of 1.0 g/m<sup>2</sup> or more in terms of solids, for example, by sizing press, tab-sizing press, blade coating, or air knife coating.

(6) After being made, paper which constitutes the substrate is calendered with a machine calender, a supercalender, a thermal calender or the like. Specifically, the substrate is preferably subjected to, for example, the thermal calendering described or exemplified in Japanese Patent Kokai No. 60-126397.

The ink jet recording sheet according to the second aspect of the invention comprises a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, said paper having a Cobb sizing degree (at a contact time with pure water of 30 seconds) of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup> as measured by the water absorption test by Cobb sizing degree method prescribed in JIS P8140.

The substrate used in the second aspect of the invention has a Cobb sizing degree of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup>, preferably 2.0 g/m<sup>2</sup> to 13.0 g/m<sup>2</sup>, more preferably 2.0 g/m<sup>2</sup> to 11.0 g/m<sup>2</sup>. When its Cobb sizing degree is less than 1.0 g/m<sup>2</sup>, the adhesion of the ink-receiving layer formed on the substrate is undesirably low. When the Cobb sizing degree is more than 15.0 g/m<sup>2</sup>, the effect of reducing the waviness after image recording is undesirably not sufficient.

There are various methods for obtaining the substrate having a Cobb sizing degree of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup> which is used in the present invention. They are roughly divided into the following two groups.

(1) Methods in which the amount of a sizing agent incorporated and the amount of a surface sizing agent applied are varied in the production of the substrate. In these methods, the penetrability of a liquid into the substrate is controlled by varying the wettability of pulp fiber in the substrate or on the substrate surface.

(2) Methods in which the void structure of the substrate is changed. The Lucas-Washburn equation is well known as a model equation expressing the penetration of a liquid into capillaries. This equation shows that the depth of penetration of the liquid is proportional to time and the square root of radius of the capillary and is inversely proportional to the square root of viscosity of the liquid. That is, another method for achieving the object of the present invention is a method of reducing the voids of the substrate (the radius of the capillary) by adjusting various paper making conditions as follows: pulp which can easily be made into denser paper, for example, hardwood pulp composed of short fibers and suited for producing paper with smooth surface is used in a proportion of 60% by weight or more, preferably 75% by weight or more, based on the weight of a pulp mixture to be used; pulp beating conditions are properly chosen; a polymer is added to a pulp slurry; multiplaten wet pressing is employed; a surface sizing agent or a water-soluble polymer is added in a coating equipment on the route; and after paper making, the paper is calendered with a machine calender, supercalender, thermal calender or the like.

The ink jet recording sheet according to the third aspect of the invention comprises a substrate made of paper com-

posed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, said paper having an unevenness index Rpy of 150 mV or less as measured under the conditions described hereinafter and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6 µm or less as measured with a tracer type three-dimensional surface roughness meter.

The "unevenness index" (Rpy) referred to in the third aspect of the present invention is defined as follows.

A sample is let run between a pair of spherical tracers, and by using a film thickness meter which measures the variation of thickness of the sample as an electrical signal through an electrical micrometer, the variation of thickness of the sample in the machine direction is measured by scanning the sample in the machine direction at a constant rate of 1.5 m/min after adjustment of the zero point, under the condition that the sensitive range of the electrical micrometer is ±15 µm/±3 V. The hanning window and FFT are applied to the electrical signal by FFT analyzer, followed by averaging of 128 times of integration, whereby the power spectrum (unit: mV<sup>2</sup>) is obtained. The obtained power value is integrated from 2 to 25 Hz, multiplied by 2/3 and then raised to the one-half power. The thus determined value (unit: mV) is the unevenness index (Rpy).

Concretely, Rpy is determined as follows. The sample is let run between a pair of spherical tracers, about 5 mm in diameter, with a measuring pressure of about 30 g/stroke, and the variation of thickness of the sample is measured by scanning the sample in the machine direction at a constant rate of 1.5 m/min after adjustment of the zero point, under the condition of sensitivity range of electrical micrometer of ±15 µm/±3 V, by using a film thickness meter mfd. by Anritsu Corp. which measures the thickness variation as an electrical signal through an electrical micrometer. The power spectrum is obtained by the electrical signal applying hanning window and FFT by the FFT analyzer CF-300 mfd. by Ono Sokki K.K. (input signal AC: ±10 mV; sampling at 512 points) in the frequency region of 0 - 50 Hz, and the linear scale power spectrum (unit: mV) is determined by averaging of 128 times of integration. The square of the linear scale power value in the frequency region of 2 - 25 Hz is integrated and the obtained value is multiplied by 2/3 and raised to the one-half power. The other frequency analytical conditions follow the initial setting conditions of the FFT analyzer CF-300.

The center plane average roughness in machine direction in the whole wavelength region (SRa) measured with a tracer type three-dimensional surface roughness meter in the third aspect of the invention is defined by the following equation 1:

$$SRa = \frac{1}{Sa} \int_0^{Wx} \int_0^{Wy} |f(x,y)| dx dy \quad (1)$$

wherein Wx is the length of sample surface region in the X-axis direction (the machine direction), Wy is the length of sample surface region in the Y-axis direction (the direction perpendicular to the machine direction), and Sa is the area of the sample surface region.

Concretely, SRa can be determined by using a SE-3AK meter and a SPA-11 analyzer which are manufactured by Kosaka Laboratory, Ltd., as a tracer type three-dimensional surface roughness meter and a three-dimensional roughness analyzer, respectively, under the following conditions: cut-off value = 0.8 mm, Wx = 20 mm, Wy = 8 mm, and hence Sa = 160 mm<sup>2</sup>. Data processing in the X-axis direction is carried out by sampling at 500 points, and scanning in the Y-axis direction is carried out in 17 lines or more.

The substrate used in the third aspect of the invention has an unevenness index Rpy specified above of 150 mV or less, preferably 140 mV or less, more preferably 130 mV or less. Investigation by the present inventors made it clear that specifically, the substrate having an unevenness index Rpy of 150 mV or less can be obtained by adopting any of, preferably a combination of two or more of, more preferably a combination of three or more of, most preferably a combination of four or more of, the methods (1) to (4) and (6) described above as to the first aspect of the invention.

In addition, the substrate used in the third aspect of the invention has a center plane average roughness SRa defined by the equation 1 of 1.6 µm or less, preferably 1.4 µm or less, more preferably 1.2 µm or less. Investigation by the present inventors made it clear that specifically, the substrate having a center plane average roughness SRa of 1.6 µm or less can be obtained by adopting any of, preferably a combination of two or more of, more preferably a combination of three or more of, the following methods.

(1) As the natural pulp, sulfite pulp (preferably hardwood sulfite pulp) suitable for producing paper with smooth surface is used in a high proportion. Specifically, the hardwood sulfite pulp described or exemplified in Japanese Patent Kokai No. 60-67940 is used in a proportion of 30% by weight or more, preferably 50% by weight or more, based on the weight of a pulp mixture to be used.

(2) Wet re-press is employed in the course of drying wet paper. Specifically, the wet paper is subjected to multi-platen wet repress such as that described or exemplified in Japanese Patent Kokai No. 3-29945.

(3) Any of various water-soluble polymers, hydrophilic colloids or polymer latices may be incorporated into or

applied on the substrate. Specifically, any of various water-soluble polymers, hydrophilic colloids or polymer latices may be incorporated into or applied on the substrate in an amount of 1.0 g/m<sup>2</sup> or more in terms of solids, for example, by sizing press, tab-sizing press, blade coating, or air knife coating.

(4) After being made, paper which constitutes the substrate is subjected to at least two series of calenderings with a machine calender, a supercalender, a thermal calender, etc. Specifically, the paper is preferably subjected to, for example, machine calendering and/or thermal machine calendering as first-series calendering(s), followed by optionally machine calendering and then the thermal soft calendering described or exemplified in Japanese Patent Kokai No. 4-110939, as second-series calenderings.

As the pulp which constitutes the substrate used for carrying out each of the first, second and third aspects of the present invention, natural pulp properly selected as described above is advantageously used. As the natural pulp, there is used wood pulp such as softwood pulp, hardwood pulp or a mixture thereof, which has been subjected to a conventional bleaching treatment with chlorine, hypochlorite, chlorine dioxide or the like, alkali extraction or alkali treatment, and optionally oxidation bleaching with hydrogen peroxide, oxygen or the like, or a combination of these treatments. Various pulps such as craft pulp, sulfite pulp, soda pulp, etc. can be used.

Various additives may be incorporated into the substrate used for carrying out the present invention, in the preparation of a pulp slurry. It is advantageous to incorporate, for example, the following additives in proper combination: sizing agents such as fatty acids and/or metallic salts of fatty acids, the alkyl ketene dimer emulsion or epoxidized higher fatty acid amides described or exemplified in Japanese Patent Kokoku No. 62-7534, alkenyl- or alkylsuccinic anhydride emulsions, rosin derivatives, etc.; dry strength agents such as anionic, cationic or ampholytic polyacrylamide, polyvinyl alcohols, cationized starch, vegetable galactomannan, etc.; wet strength agents such as polyamine-polyamido-epichlorohydrin resin, etc.; fillers such as clay, kaolin, calcium carbonate, titanium oxide, etc.; fixing agents such as water-soluble aluminum salts (e.g. aluminum chloride and aluminum sulfate), etc.; pH adjustors such as sodium hydroxide, sodium carbonate, sulfuric acid, etc.; and the color pigments, dyes, fluorescent brighteners and the like, which are described or exemplified in Japanese Patent Kokai Nos. 63-204251 and 1-266537, etc.

A composition consisting of any of various water-soluble polymers, hydrophilic colloids or polymer latices, an anti-static agent and other additives may be incorporated into or applied on the substrate used for carrying out the present invention, by, for example, sizing press, tab-sizing press, blade coating, or air knife coating. It is advantageous to incorporate the following in proper combination: water-soluble polymers or hydrophilic colloids, such as the starch-based polymers described or exemplified in Japanese Patent Kokai No. 1-266537, polyvinyl alcohol-based polymers, gelatin-based polymers, polyacrylamide-based polymers, cellulose-based polymers, etc.; emulsions and latices, such as petroleum resin emulsions, emulsions or latices of the copolymers having as components at least ethylene and acrylic acid (or methacrylic acid) which are described or exemplified in Japanese Patent Kokai Nos. 55-4027 and 1-180538, emulsions or latices of styrene-butadiene, styrene-acryl, vinyl acetate-acryl, ethylene-vinyl acetate and butadiene-methyl methacrylate copolymers and their carboxy-modified versions, etc.; antistatic agents such as alkali metal salts (e.g. sodium chloride and potassium chloride), alkaline earth metal salts (e.g. calcium chloride and barium chloride), colloidal metal oxides (e.g. colloidal silica), organic antistatic agents (e.g. polystyrene sulfonates), etc.; fillers such as clay, kaolin, calcium carbonate, talc, barium sulfate, titanium oxide, etc.; pH adjustors such as hydrochloric acid, phosphoric acid, citric acid, sodium hydroxide; and the above-exemplified color pigments, dyes, fluorescent brighteners.

The thickness of the substrate used for carrying out the present invention is not particularly limited. The basis weight of the substrate may be properly chosen in the range of 20 to 300 g/m<sup>2</sup>, preferably 80 to 280 g/m<sup>2</sup>, more preferably 100 to 250 g/m<sup>2</sup>.

The ink jet recording sheet of the present invention is of a coated type and comprises the above-mentioned substrate and an ink-receiving layer formed thereon. The term "ink-receiving layer" used in the present specification means, for example, a layer composed mainly of at least one pigment and at least one binder and having voids into which a solvent contained in ink penetrates and holds or absorbs the solvent, a layer composed mainly of at least one high-molecular weight substance which dissolves or swells in a solvent contained in ink. Each of these layers may be composed of a single layer, two or more layers, or a combination of a pigment layer and a polymer layer without any problem, as the ink-receiving layer used in the present invention.

When such an ink-receiving layer is formed on the substrate used in the first or second aspect of the invention, it can be made uniform. When images are recorded on the ink-receiving layer surface with an ink jet printer, there can be obtained recording sheet which is excellent in the coloration and sharpness of the recorded images and has no sheet waviness even after drying of the recorded images.

Although the reason why no waviness is caused is not apparent, the cause of waviness is guessed as follows: in general, when water penetrates into a recording sheet, pulp constituting the sheet is swollen and undergoes stress relaxation, so that local unevenness of the sheet surface caused by re-drying remains. However, it is conjectured that when paper having a density of sheet of 1.01 g/cm<sup>3</sup> or more is prepared as a substrate, there is almost no space between fibers of pulp, so that the degree of the local unevenness is very low. It is also conjectured that in the case of

a substrate having very low water absorption properties, i.e., a Cobb sizing degree in the range of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup> like the substrate used in the second aspect of the invention, no waviness is caused because the swelling and stress relaxation of pulp are very slight, so that the degree of the local unevenness is very low.

In addition, when the ink-receiving layer is formed on the substrate used in the third aspect of the invention, it can be made smooth and uniform. In this case, when ink is deposited on the ink-receiving layer surface by means of an ink jet printer, a recorded dot close to a true circle can be obtained because the ink-receiving layer surface formed by coating is uniform, so that the ink spreads uniformly in the direction of the ink-receiving layer surface. The reason is guessed as follows: the surplus ink penetrates uniformly in the direction of thickness of the substrate from the ink-receiving layer surface. On the other hand, when the ink-receiving layer is formed on a substrate having thickness unevenness and average roughness outside their respective ranges specified in the present invention, the ink-receiving layer surface tends to have non-uniformity of coating, so that ink spreads in the direction of the recording surface in a nonuniform proportion. Consequently, a recorded dot unlike a true circle is obtained, and the sharpness of images is not sufficient because the spread of the ink is different in different places. Moreover, the penetration of the ink into the substrate becomes irregular, so that the circumference of dots are not sharp, resulting in a deteriorated sharpness of images.

In an embodiment of the present invention in which the ink-receiving layer composed mainly of at least one pigment and at least one binder is used, the pigment may be any conventional pigment. The pigment includes, for example, inorganic or organic pigments such as silicas (e.g. colloidal silica and amorphous silica), aluminas or alumina hydrates (e.g. alumina sol, colloidal alumina, cationic aluminium oxide or hydrotates thereof, and pseudo-boehmite), aluminum silicate, magnesium silicate, magnesium carbonate, light calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin white, diatomaceous earth, calcium silicate, aluminum hydroxide, lithopone, zeolite, hydrated halloysite, magnesium hydroxide, styrene plastic pigments, acrylic plastic pigments, polyethylenes, microcapsules, urea resins, melamine resins, etc.

Of the inorganic pigments exemplified above, porous inorganic pigments such as porous synthetic amorphous silica, porous magnesium carbonate, porous alumina, etc. are preferable. In particular, there can be preferably used porous synthetic amorphous silica or porous alumina hydrate, which has a large capacity of pore. Non-porous inorganic pigments can also be used as the pigment for the ink-receiving layer used in the present invention because particles of the non-porous inorganic pigment are aggregated during preparation of a coating solution and further aggregated during coating and drying to form a porous coating surface. The porous inorganic pigments and the non-porous inorganic pigments may be used at the same time without any problem.

The binder includes, for example, polyvinyl alcohols and derivatives thereof, polyvinyl acetates, oxidized starch, etherified starch, cellulose derivatives (e.g. carboxymethyl cellulose and hydroxyethyl cellulose), casein, gelatin, soybean protein, silyl-modified polyvinyl alcohols, maleic anhydride resins, latices of conjugated diene type copolymers (e.g. styrene-butadiene copolymers and methyl methacrylate-butadiene copolymers), latices of acrylic polymers (e.g. polymers or copolymers of acrylic esters and methacrylic esters, and polymers or copolymers of acrylic acid and methacrylic acid), latices of vinyl copolymers (e.g. ethylene-vinyl acetate copolymers), latices of functional group-modified polymers obtained by modifying any of the above various polymers by the use of a monomer containing the functional group such as carboxyl group, aqueous binders of thermosetting synthetic resins (e.g. melamine resins and urea resins), and synthetic resin binders (e.g. polymethyl methacrylates, polyurethane resins, unsaturated polyester resins, vinyl chloride-vinyl acetate copolymers, polyvinyl butyrals, and alkyd resins). These binders may be used singly or as a mixture thereof. For dye fixing, conventional cationic resins may be used in combination with the binders.

The total amount of the binder(s) used can be properly adjusted depending on characteristics of a desired ink jet recording sheet. It is usually 5 to 60 parts by weight per 100 parts by weight of the pigment(s). In addition, the ink-receiving layer may properly contain other additives such as pigment dispersants, thickening agents, fluidity improvers, defoaming agents, foam-inhibitors, mold release agents, foaming agents, penetrating agents, color pigments, dyes, fluorescent brighteners, ultraviolet absorbers, anti-oxidants, antiseptics, mildew-proofing agents, water-proofing agents, wet strength agents, dry strength agents, etc.

In another embodiment of the present invention in which there is used the ink-receiving layer composed mainly of at least one high-molecular weight substance which dissolves or swells in a solvent contained in ink, the high-molecular weight substance includes, for example, polyvinyl alcohols, polyvinyl acetates, oxidized starch, etherified starch, gelatin and its derivatives, cellulose derivatives (e.g. carboxymethyl cellulose and hydroxyethyl cellulose), various ink-absorbing polymers (e.g. polyvinyl pyrrolidones, polyethylene oxides, acrylic polymers, and vinyl acetal polymers), etc. These high-molecular weight substances may be used singly or as a mixture thereof. A multi-layer structure containing the high-molecular weight substances may also be used as the ink-receiving layer used in the present invention.

For forming the ink-receiving layer by coating, various coating equipments such as blade coater, roll coater, air-knife coater, bar coater, rod coater, gate roll coater, curtain coater, short-dwell coater, gravure coater, flexo-gravure coater, sizing press, slide hopper type equipments, etc. can be used in on-machine or off-machine coating.

After the coating, finishing may be carried out with a calender such as a machine calender, thermal calender, supercalender, soft calender or the like.

Although the thickness of the ink-receiving layer is not particularly limited, the coating amount is preferably 0.5 g/m<sup>2</sup> to 60 g/m<sup>2</sup>.

On the side of substrate used in the present invention which is reverse to the ink-receiving layer side, various back coat layers may be formed in order to improve the antistatic properties, sheet feed ability, curl-preventing properties, writability, starchability, etc. The back coat layers may contain a proper combination of inorganic antistatic agents, organic antistatic agents, hydrophilic binders, latices, hardening agents, pigments, lubricants, matting agents, surfactants, etc.

The ink referred to in the present specification is a recording liquid comprising at least one coloring agent, at least one liquid medium and other additives. The coloring agent includes, for example, water-soluble dyes and disperse dyes, such as direct dyes, acid dyes, basic dyes, reactive dyes, food dyes, etc.; color pigments; and carbon black.

The solvent in the ink includes, for example, water and water-soluble various organic solvents, e.g., alkyl alcohols having 1 to 4 carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, isobutanol, etc.; amides such as dimethylformamide, dimethylacetamide, etc.; ketones or ketone alcohols, such as acetone, diacetone alcohols, etc.; ethers such as tetrahydrofuran, dioxane, etc.; polyalkylene glycols such as polyethylene glycols, polypropylene glycols, etc.; alkylene glycols having 2 to 6 alkylene groups, such as ethylene glycol, propylene glycol, butylene glycol, triethylene glycol, 1,2,6-hexanetriol, thiodiglycol, hexylene glycol, diethylene glycol, etc.; and glycerol, lower alkyl ethers of polyhydric alcohols (e.g. ethylene glycol methyl ether, diethylene glycol methyl (or ethyl) ether, and triethylene glycol monomethyl ether), etc. Of these various water-soluble organic solvents, polyhydric alcohol (e.g. diethylene glycol) and lower alkyl ethers of polyhydric alcohols (e.g. triethylene glycol monomethyl ether and triethylene glycol monoethyl ether) are preferable. The other additives include, for example, pH adjustors, sequestering agents, mildew-proofing agents, viscosity adjustors, surface tension adjustors, wetting agents, surfactants, and rust preventives.

The ink jet recording sheet of the present invention can be used not only as an ink jet recording sheet for aqueous ink but also as any recording sheet for ink which is liquid at the time of recording. Such a recording sheet includes, for example, receiving sheets for heat transfer recording which are used by heating an ink-coated sheet obtained by applying heat-meltable ink composed mainly of, for example, a heat-meltable substance and a dye or pigment on a thin support (e.g. a resin film, high-density paper, or synthetic paper), from the backside to melt and transfer the ink; ink jet recording sheets for performing recording by heat-melting heat-meltable ink into droplets and ejecting the droplets; ink jet recording sheets for ink obtained by dissolving an oil-soluble dye in a solvent; ink jet recording sheets for ink obtained by dispersing a color pigment in an organic solvent; and image-receiving sheets suitable for light-sensitive and pressure-sensitive donor sheets obtained by using micro-capsules containing a photopolymerizable monomer and a colorless or color dye or pigment.

A point common to these recording sheets is that ink is liquid at the time of recording. The liquid ink penetrates or diffuses into the ink-receiving layer of the recording sheet in the direction of depth or the horizontal direction before hardening, solidification or fixing. The above-exemplified various recording sheets are required to have absorbing properties suitable for each method, and the ink jet recording sheet of the present invention may be used as any of the above-exemplified various recording sheets without any limitation. Furthermore, the ink jet recording sheet of the present invention may be used as a recording sheet for heating and fixing a toner for electrophotographic recording which is widely used in copying machines, printers, etc.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is illustrated with reference to the following examples, which should not be construed as limiting the scope of the invention. In the examples, parts and percents are all by parts unless otherwise specified.

##### Examples 1 to 5

Mixed pulp consisting of 85% by weight of hardwood bleached kraft pulp and 15% by weight of softwood bleached sulfite pulp was beaten to each degree of beating shown in Table 1. A pulp slurry was prepared by adding 3 parts by weight of cationized starch, 0.2 part by weight of anionized polyacrylamide, 0.4 part by weight (in terms of ketene dimer) of an alkylketene dimer emulsion, and 0.4 part by weight of a polyamidoepichlorohydrin resin to 100 parts by weight of the beaten mixed pulp. The pulp slurry was formed into a web with a Fourdrinier machine, and the web was subjected to three-platen wet pressing and then treatment with a smoothing roll in the wet part, subjected to two-platen wet repress in the subsequent dry part, and then dried. In the course of the drying, a size press liquor containing 5% by weight of a carboxy-modified polyvinyl alcohol was size pressed at a rate of 20 g/m<sup>2</sup>, and the resulting product was dried so that the water content of the finally obtained paper based on bone dry weight might be 8% by weight. The thus obtained paper was subjected to machine calendering at the linear pressure shown in Table 1, to obtain a substrate for ink jet recording sheet which had a basis weight of 150 g/m<sup>2</sup> and the density shown in Table 1. All the substrates thus obtained had a Cobb sizing degree of 15 to 16 g/m<sup>2</sup>.



## Comparative Examples 1 to 3

Mixed pulp consisting of 85% by weight of hardwood bleached kraft pulp and 15% by weight of softwood bleached kraft pulp was beaten to each degree of beating shown in Table 1. To 100 parts by weight of the beaten mixed pulp were added 0.7 part by weight of amphoteric starch (Cato 3210, mfd. by Oji National Company, Ltd.) and 0.1 part by weight of an alkylketene dimer sizing agent (Size Pine K903, mfd. by Arakawa Chemical Co., Ltd.). The resulting mixture was formed into a web with a Fourdrinier machine. The web was subjected to two-platen wet pressing but not treatment with a smoothing roll in the wet part, and dried without wet re-press in the subsequent dry part. In the course of the drying, a size press liquor containing 5% by weight of a carboxy-modified polyvinyl alcohol was size pressed at a rate of 20 g/m<sup>2</sup>, and the resulting product was dried so that the water content of the finally obtained paper based on bone dry weight might be 8% by weight. The obtained paper was subjected to machine calendering at the linear pressure shown in Table 1. Thus, there were produced substrates of Comparative Examples 1 to 3 each having a basis weight of 150 g/m<sup>2</sup> and the density shown in Table 1.

(Production of ink jet recording sheets)

A coating solution having a solid content of about 10% and consisting of 5 parts by weight (in terms of solids) of alumina sol AS-3 (pseudo-boehmite, mfd. by Catalysts and Chemicals Industry Co., Ltd.), 1 part by weight (in terms of solids) of a polyvinyl alcohol MA-26 (mfd. by Shin-etsu Chemical Co. Ltd.) and water was prepared as a composition for forming an ink-receiving layer. The coating solution was applied on each substrate produced in the manner described above, with a bar coater so that the dry coating amount might be 15 g/m<sup>2</sup>. Then, the substrate was dried to produce an ink jet recording sheet.

The ink jet recording sheets thus produced in Examples and Comparative Examples were evaluated by the following evaluation method. The results obtained are summarized in Table 1.

(Waviness after image recording)

Waviness after image recording was evaluated by forming high-definition photographic images having wide hue and lightness ranges, allowing the images to stand for 24 hours, and visually evaluating the waviness of the recording surface after drying in the following five grades:

- ⊙: No waviness after image recording.
- : Almost no waviness after image recording.
- ◇: Negligible waviness after image recording.
- △: Rather large waviness after image recording.
- X: Remarkable waviness after image recording.

Table 1

Sample No.	Degree of beating mlCSF	Linear pressure at machine calendering kg/cm	density of substrate g/cm <sup>3</sup>	Waviness after image recording
Example 1	250	100	1.04	○
Example 2	250	150	1.06	⊙
Example 3	320	70	1.01	◇
Example 4	320	100	1.03	○
Example 5	320	150	1.05	⊙
Comparative Example 1	320	70	0.93	X
Comparative Example 2	400	70	0.91	X
Comparative Example 3	450	70	0.89	X

From the results shown in Table 1, it can be seen that the waviness after image recording and drying was satisfactorily reduced in the ink jet recording sheets obtained in Examples by using a substrate having a density of 1.01/cm<sup>3</sup> or

more.

#### Examples 6 to 9

5 Mixed pulp consisting of 85% by weight of hardwood bleached kraft pulp and 15% by weight of softwood bleached sulfite pulp was beaten to a degree of beating of 320 ml CSF. A pulp slurry was prepared by adding 3 parts by weight of cationized starch, 0.2 part by weight of anionized polyacrylamide, 0.2 part by weight (Example 6), 0.3 part by weight (Example 7), 0.4 part by weight (Example 8) or 0.5 part by weight (Example 9) (in terms of ketene dimer) of an alkylketene dimer emulsion, and 0.4 part by weight of a polyamido-epichlorohydrin resin to 100 parts by weight of the beaten  
10 mixed pulp. The pulp slurry was formed into a web with a Fourdrinier machine, and the web was subjected to three-platen wet pressing and then treatment with a smoothing roll in the wet part, subjected to two-platen wet re-press in the subsequent dry part, and then dried. In the course of the drying, a carboxy-modified polyvinyl alcohol solution was size pressed to adjust the amount of the solution adhered to 2.0 g/m<sup>2</sup> in terms of solids. The resulting product was dried so that the water content of the finally obtained paper based on bone dry weight might be 8% by weight. The thus obtained  
15 paper was subjected to machine calendering at a linear pressure of 60 kg/cm to obtain a substrate for ink jet recording sheet which had a basis weight of 150 g/m<sup>2</sup> and the Cobb sizing degree shown in Table 2. All the substrates thus obtained had a density of 0.98 to 1.00 g/m<sup>3</sup>.

#### Examples 10 to 12

20 Substrates for ink jet recording sheet which each had the Cobb sizing degree shown in Table 2 were produced in the same manner as in Example 8 except for using a liquor consisting of 5 parts by weight of carboxy-modified polyvinyl alcohol and 0.10 part by weight of a surface sizing agent composed of a styrene/acrylic acid copolymer (KN-500, mfd. by Harima Chemicals, Inc.), in place of the size press solution used in Example 8, and adjusting the amount of the liquor  
25 adhered to 1.0 g/m<sup>2</sup> (Example 10), 2.0 g/m<sup>2</sup> (Example 11) or 3.0 g/m<sup>2</sup> (Example 12). All the substrates had a density of 0.98 to 1.00 g/m<sup>3</sup>.

#### Comparative Examples 4 and 9

30 Substrates of Comparative Examples 4 and 9 each having the Cobb sizing degree shown in Table 2 were produced in the same manner as in Example 6 except for changing the amount of the alkylketene dimer emulsion in terms of ketene dimer to 0.1 part by weight (Comparative Example 4) or 1.0 part by weight (Comparative Example 9).

#### (Production of ink jet recording sheets)

35 A coating solution having a solid content of about 10% and consisting of 5 parts by weight (in terms of solids) of alumina sol AS-3 (pseudo-boehmite, mfd. by Catalysts and Chemicals Industry Co., Ltd.), 1 part by weight (in terms of solids) of a polyvinyl alcohol MA-26 (mfd. by Shin-etsu Chemical Co. Ltd.) and water was prepared as a composition for forming an ink-receiving layer. The coating solution was applied on each substrate produced in the manner described  
40 above, with a bar coater so that the dry coating amount might be 15 g/m<sup>2</sup>. Then, the substrate was dried to produce an ink jet recording sheet. In the substrate of Comparative Example 9, the ink-receiving layer peeled off, so that the ink jet recording sheet obtained by using this substrate could not be evaluated.

#### Comparative Examples 5 to 8

45 The same substrate as in Examples 6 to 9 were used as they were as substrates of Comparative Examples 5 to 8, respectively, without forming an ink-receiving layer.

The ink jet recording sheets thus produced in Examples 6 to 12 and Comparative Examples 4 to 9 were evaluated by the following evaluation methods. The results obtained are summarized in Table 2.

#### (Sharpness of image)

55 Sharpness of image was evaluated by forming a high-definition photographic image and visually observing the overflow and run of ink. An excellent ink jet recording sheet was rated as (marked by) ○, an ink jet recording sheet equal to a conventional one as △, and an unusable ink jet recording sheet as X.

(Waviness after image recording)

Waviness after image recording was evaluated by forming high-definition photographic images having wide hue and lightness ranges, allowing the images to stand for 24 hours, and visually evaluating the waviness of the recording surface after drying in the following five grades:

- ◎: No waviness after image recording.  
 ○: Almost no waviness after image recording.  
 ◇: Negligible waviness after image recording.  
 △: Rather large waviness after image recording.  
 X: Remarkable waviness after image recording.  
 Not evaluable

Table 2

Sample No.	Cobb sizing degree of substrate g/m <sup>2</sup>	Sharpness of image	Waviness after image recording
Example 6	14.8	○	◇
Example 7	12.5	○	○
Example 8	10.1	○	◎
Example 9	8.2	○	◎
Example 10	8.8	○	◎
Example 11	5.7	○	◎
Example 12	2.3	○	◎
Comparative Example 4	16.4	△	X
Comparative Example 5	14.5	X	◎
Comparative Example 6	12.8	X	◎
Comparative Example 7	10.6	X	◎
Comparative Example 8	9.2	X	◎
Comparative Example 9	0.9	Not evaluable	Not evaluable

From the results shown in Table 2, it can be seen that ink jet recording sheets which were excellent in image sharpness and had satisfactorily reduced waviness after image recording and drying were obtained in Examples in which an ink-receiving layer was formed on a substrate having a Cobb sizing degree of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup>.

#### Examples 13 to 21

Mixed pulp consisting of 50% by weight of hardwood bleached kraft pulp, 35% by weight of hardwood bleached sulfite pulp and 15% by weight of softwood bleached sulfite pulp was beaten to each fiber length shown in Table 3. A pulp slurry was prepared by adding 3 parts by weight of cationized starch, 0.2 part by weight of anionized polyacrylamide, 0.4 part by weight (in terms of ketene dimer) of an alkylketene dimer emulsion, 0.4 part by weight of a polyamido-epichlorohydrin resin and proper amounts of a fluorescent brightener, a blue dye and a red dye to 100 parts by weight of the beaten mixed pulp. The pulp slurry was formed into a web with a Fourdrinier machine, and the web was subjected to three-platen wet pressing and then treatment with a smoothing roll in the wet part, subjected to two-platen wet repress in the subsequent dry part, and then dried. In the course of the drying, a size press liquor consisting of 4 parts by weight of a carboxy-modified polyvinyl alcohol, 0.05 part by weight of a fluorescent brightener, 4 parts by weight of sodium chloride and 92 parts by weight of water was size pressed at a rate of 20 g/m<sup>2</sup>, and the resulting product was dried so that the water content of the finally obtained paper based on bone dry weight might be 8% by weight. The thus obtained paper was subjected to machine calendering at the linear pressure shown in Table 3. Then, the paper was either subjected or not to thermal soft calendering at a temperature of 200°C and a linear pressure of 200 kg/cm in accordance with the instruction given in Table 3, to obtain a substrate for ink jet recording sheet which had a basis weight of 150 g/m<sup>2</sup> and the unevenness index Rpy value and center plane average roughness SRa value shown in

Table 3.

## Comparative Examples 10 to 15

Substrates of Comparative Examples 10 to 15 each having a basis weight of 150 g/m<sup>2</sup> and the unevenness index Rpy value and center plane average roughness S<sub>Ra</sub> value shown in Table 3 were produced by treatments under the conditions shown in Table 3, in the same manner as in Examples 13 to 21 except for using mixed pulp consisting of 90% by weight of hardwood bleached kraft pulp and 10% by weight of softwood bleached kraft pulp, in place of the mixed pulp used in Examples 13 to 21.

## (Production of ink jet recording sheets)

A coating solution having a solid content of about 10% and consisting of 5 parts by weight (in terms of solids) of alumina sol AS-3 (pseudo-boehmite, mfd. by Catalysts and Chemicals Industry Co., Ltd.), 1 part by weight (in terms of solids) of a polyvinyl alcohol PVA117 (mfd. by Kuraray Co., Ltd.) and water was prepared as a composition for forming an ink-receiving layer. The coating solution was applied on each substrate produced in the manner described above, with a bar coater so that the dry coating amount might be 15 g/m<sup>2</sup>. Then, the substrate was dried to produce an ink jet recording sheet.

The ink jet recording sheets produced in Examples 13 to 21 and Comparative Examples 10 to 15 were evaluated by the following evaluation methods. The results obtained are summarized in Table 3.

## (Quality of image)

Quality of image was evaluated by forming sharp and high-definition photographic images having wide hue and lightness ranges, and evaluating the result of visual observation of the images in the following five grades:

- ⊙: Very excellent quality of image.
- : Excellent quality of image.
- ◇: Good quality of image.
- △: Rather good quality of image.
- X: Bad quality of image.

## (Uniformity of coating layer)

Uniformity of coating layer was evaluated by visually judging the nonuniformity of coating of a surface printed with 50% dots of 720 dpi black ink, in the following four grades:

- ⊙: No or almost no nonuniformity of coating.
- : Slight nonuniformity of coating.
- △: Some but practically allowable nonuniformity of coating.
- X: Practically unallowable nonuniformity of coating.

Table 3

Sample No.	Pulp fiber length after beating mm	Linear pressure at machine calendering kg/cm	Thermal soft calendering	Rpy mV	S <sub>Ra</sub> μm	Quality of image	Uniformity of coating layer
Example 13	0.55	70	None	140	1.30	○	○
Example 14	0.60	70	Carried out	125	1.15	⊙	⊙
Example 15	0.65	70	None	145	1.40	○	○
Example 16	0.65	70	Carried out	130	1.20	⊙	○
Example 17	0.65	90	None	135	1.25	○	○
Example 18	0.65	150	Carried out	120	1.18	⊙	⊙

Table 3 (continued)

Sample No.	Pulp fiber length after beating mm	Linear pressure at machine calendering kg/cm	Thermal soft calendering	Rpy mV	SRa $\mu\text{m}$	Quality of image	Uniformity of coating layer
Example 19	0.70	70	Carried out	135	1.38	○	○
Example 20	0.75	90	None	145	1.42	◇	○
Example 21	0.85	150	Carried out	150	1.58	◇	△
Comparative Example 10	0.80	50	None	165	1.75	X	X
comparative Example 11	0.80	90	None	160	1.68	△	△
Comparative Example 12	0.85	70	Carried out	160	1.76	X	△
Comparative Example 13	0.85	70	None	185	1.95	X	X
Comparative Example 14	0.95	90	Carried out	170	2.12	X	X
Comparative Example 15	0.95	90	None	195	2.10	X	X

From the results shown in Table 3, it can be seen that ink jet recording sheets satisfactory in both quality of image and uniformity of coating layer could be obtained in Examples 13 to 21 in which each substrate having an Rpy value of 150 mV or less and an SRa value of 1.6  $\mu\text{m}$  or less was used.

#### Examples 22 to 25

Mixed pulp consisting of 50% by weight of hardwood bleached kraft pulp, 35% by weight of hardwood bleached sulfite pulp and 15% by weight of softwood bleached sulfite pulp was beaten to each fiber length shown in Table 4. A pulp slurry was prepared by adding 3 parts by weight of cationized starch, 0.2 part by weight of anionized polyacrylamide, 0.4 part by weight (in terms of ketene dimer) of an alkylketene dimer emulsion, 0.4 part by weight of a polyamido-epichlorohydrin resin and proper amounts of a fluorescent brightener, a blue dye and a red dye to 100 parts by weight of the beaten mixed pulp. The pulp slurry was formed into a web with a Fourdrinier machine, and the web was subjected to three-platen wet pressing and then treatment with a smoothing roll in the wet part, subjected to two-platen wet press in the subsequent dry part, and then dried. In the course of the drying, a size press liquor consisting of 8 parts by weight of a carboxy-modified polyvinyl alcohol, 0.05 part by weight of a fluorescent brightener, 4 parts by weight of sodium chloride and 88 parts by weight of water was size pressed at a rate of 25 g/m<sup>2</sup>, and the resulting product was dried so that the water content of the finally obtained paper based on bone dry weight might be 8% by weight. The thus obtained paper was subjected to machine calendering at the linear pressure shown in Table 4. Then, the paper was either subjected or not to thermal soft calendering at a temperature of 200°C and a linear pressure of 200 kg/cm in accordance with the instruction given in Table 4, to obtain a substrate for ink jet recording sheet which had a basis weight of 150 g/m<sup>2</sup> and the values of density, Cobb sizing degree, unevenness index Rpy and center plane average roughness SRa which are shown in Table 4.

#### (Production of ink jet recording sheets)

A coating solution having a solid content of about 10% and consisting of 5 parts by weight (in terms of solids) of alumina sol AS-3 (pseudo-boehmite, mfd. by Catalysts and Chemicals Industry Co., Ltd.), 1 part by weight (in terms of solids) of a polyvinyl alcohol PVA117 (mfd. by Kuraray Co., Ltd.) and water was prepared as a composition for forming an ink-receiving layer. The coating solution was applied on each substrate produced in the manner described above, with a bar coater so that the dry coating amount might be 15 g/m<sup>2</sup>. Then, the substrate was dried to produce an ink jet recording sheet.

The ink jet recording sheet of Examples 15, 16, and 22 to 25 and Comparative Examples 10 to 13 were evaluated by the evaluation methods described above. The results obtained are summarized in Table 4.

Table 4

Sample No.	Fiber length of beaten pulp mm	Linear pressure at machine calendering kg/cm	Thermal soft calendering	Density g/cm <sup>3</sup>	Cobb sizing degree g/m <sup>2</sup>	Rpy mV	SRa $\mu$ m	Quality of image	Uniformity of coating layer	Waviness after image recording
Example 15	0.65	70	None	0.99	15.8	145	1.40	○	○	◇
Example 16	0.65	70	Carried out	1.01	15.8	130	1.20	◎	○	○
Example 22	0.65	70	None	0.99	10.7	135	1.25	○	○	○
Example 23	0.65	70	Carried out	1.02	11.1	120	1.18	◎	◎	◎
Example 24	0.65	90	None	1.02	11.1	135	1.38	○	○	◎
Example 25	0.65	150	Carried out	1.03	11.8	145	1.42	◇	○	◎
Comparative Example 10	0.80	50	None	0.91	15.8	165	1.75	×	×	△
Comparative Example 11	0.80	90	None	0.98	16.0	160	1.68	△	△	△
Comparative Example 12	0.85	70	Carried out	0.99	15.9	160	1.76	×	△	△
Comparative Example 13	0.85	70	None	0.92	15.7	185	1.95	×	×	×

From the results shown in Table 4, it can be seen that an ink jet recording sheets satisfactory in both quality of

image and uniformity of coating layer could be obtained in Examples 15, 16, and 22 to 25 in which each substrate having an Rpy value of 150 mV or less and an SRa value of 1.6  $\mu\text{m}$  or less was used. It can also be seen that excellent ink jet recording sheets free from waviness even after image recording and drying could be obtained when there was used each substrate having a density of 1.01  $\text{g/cm}^3$  or more or a Cobb sizing degree of 1.0  $\text{g/m}^2$  to 15  $\text{g/m}^2$  in addition to the above-mentioned Rpy value and SRa value. Furthermore, it can be seen that ink jet recording sheets satisfactory in all the evaluation items could be obtained particularly when there was used each substrate satisfying all of the above mentioned conditions.

As shown in Table 1, an ink jet recording sheet obtained by coating an ink-receiving layer on the substrate for ink jet recording sheet used in the first aspect of the invention, i.e., the substrate having a density of 1.01  $\text{g/cm}^3$  or more is an excellent coated type ink jet recording sheet having no waviness even after image recording and drying.

As shown in Table 2, an ink jet recording sheet obtained by coating an ink-receiving layer on the substrate for ink jet recording sheet used in the second aspect of the invention, i.e., the substrate having a Cobb sizing degree of 1.0  $\text{g/m}^2$  to 15.0  $\text{g/m}^2$  is an excellent coated type ink jet recording sheet which is excellent in image sharpness and has no waviness even after image recording and drying.

As shown in Table 3, an ink jet recording sheet obtained by coating an ink-receiving layer on the substrate for ink jet recording sheet used in the third aspect of the invention, i.e., the substrate having an unevenness in thickness in machine direction (Rpy) of 150 mV or less and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6  $\mu\text{m}$  or less as measured with a tracer type three-dimensional surface roughness meter, is an excellent coated type ink jet recording sheet which has no nonuniformity of coating of the ink-receiving layer surface and is excellent in quality of image.

As shown in Table 4, an ink jet recording sheet obtained by coating an ink-receiving layer on a substrate for ink jet recording sheet which satisfies the conditions specified in the above three aspects of the invention, i.e., a substrate having a density of 1.01  $\text{g/cm}^3$  or more, a Cobb sizing degree of 1.0  $\text{g/m}^2$  to 15.0  $\text{g/m}^2$ , an unevenness in thickness in machine direction (Rpy) of 150 mV or less and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6  $\mu\text{m}$  or less as measured with a tracer type three-dimensional surface roughness meter, is an excellent coated type ink jet recording sheet which is excellent in image sharpness, has no waviness even after image recording and drying, has no nonuniformity of coating of the ink-receiving layer surface, and is excellent in quality of image.

## Claims

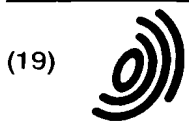
1. An ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, said substrate having a density of sheet of 1.01  $\text{g/cm}^3$  or more as measured by the method prescribed in JIS P8118.
2. An ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, said substrate having a Cobb sizing degree of 1.0  $\text{g/m}^2$  to 15.0  $\text{g/m}^2$  as measured by the water absorption test by Cobb sizing degree method prescribed in JIS P8140.
3. An ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, said substrate having an unevenness in thickness in machine direction specified below (Rpy) of 150 mV or less and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6  $\mu\text{m}$  or less as measured with a tracer type three-dimensional surface roughness meter:

Unevenness index Rpy: A sample is let run between a pair of spherical tracers, and by using a film thickness meter which measures the variation of thickness of the sample as an electrical signal through an electrical micrometer, the variation of thickness of the sample in the machine direction is measured by scanning the sample in the machine direction at a constant rate of 1.5 m/min after adjustment of the zero point, under the condition that the sensitive range of the electrical micrometer is  $\pm 15 \mu\text{m}/\pm 3 \text{ V}$ . The hanning window and FFT are applied to the electrical signal by FFT analyzer, followed by averaging of 128 times of integration, whereby the power spectrum (unit:  $\text{mV}^2$ ) is obtained. The obtained power value is integrated in the frequency region of 2 to 25 Hz, multiplied by 2/3 and then raised to the one-half power. The thus determined value (unit: mV) is the unevenness index (Rpy).

4. The ink jet recording sheet according to claim 2, wherein the density of sheet of the substrate is 1.01  $\text{g/cm}^3$  or more as measured by the method prescribed in JIS P8118.

5. The ink jet recording sheet according to claim 3, wherein the density of sheet of the substrate is  $1.01 \text{ g/cm}^3$  or more as measured by the method prescribed in JIS P8118.
6. The ink jet recording sheet according to claim 3, wherein the Cobb sizing degree of the substrate is  $1.0 \text{ g/m}^2$  to  $15.0 \text{ g/m}^2$  as measured by the water absorption test by Cobb sizing degree method prescribed in JIS P8140.
7. The ink jet recording sheet according to claim 3, wherein the density of sheet of the substrate is  $1.01 \text{ g/cm}^3$  or more as measured by the method prescribed in JIS P8118, and the Cobb sizing degree of the substrate is  $1.0 \text{ g/m}^2$  to  $15.0 \text{ g/m}^2$  as measured by the water absorption test by Cobb sizing degree method prescribed in JIS P8140.
8. The ink jet recording sheet according to any one of claims 1 to 7, wherein the ink-receiving layer contains at least porous synthetic amorphous silica or porous alumina hydrate.
9. The ink jet recording sheet according to claim 8, wherein the porous alumina hydrate is pseudo-boehmite.





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Office européen des brevets



(11) **EP 0 887 199 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
28.07.1999 Bulletin 1999/30

(51) Int. Cl.<sup>6</sup>: **B41M 5/00**

(43) Date of publication A2:  
30.12.1998 Bulletin 1998/53

(21) Application number: **98111534.8**

(22) Date of filing: **23.06.1998**

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(30) Priority: **26.06.1997 JP 17016897**  
**26.06.1997 JP 17016997**  
**26.06.1997 JP 17017097**

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(54) **Ink jet recording sheet**

(57) The present invention provides an ink jet recording sheet which is excellent in image sharpness, has no waviness even after image recording and drying, has no nonuniformity of coating of the ink-receiving layer surface, and is excellent in quality of image, when the sheet is used in an ink jet recording method using aqueous ink. This object has been achieved by an ink jet recording sheet comprising a substrate made of paper composed mainly of natural pulp and an ink-receiving layer coated on at least one side of the substrate, wherein the ink-receiving layer is formed on the substrate having a density of 1.01 g/cm<sup>3</sup> or more, a Cobb sizing degree of 1.0 g/m<sup>2</sup> to 15.0 g/m<sup>2</sup>, an unevenness in thickness in machine direction (Rpy) of 150 mV or less and a center plane average roughness in machine direction in the whole wavelength region (SRa) of 1.6 µm or less as measured with a tracer type three-dimensional surface roughness meter.

EP 0 887 199 A3



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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 11 1534

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.C1.6)
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A	US 5 589 259 A (K.HOSOI ET AL.) 31 December 1996 * column 3, line 11 - line 52 * * column 5, line 23 - column 6, line 36 * * column 9, line 23 - line 66 * * claims 1-4; examples 1-6,8,9 * * tables 1-3 *	1-9	
A	PATENT ABSTRACTS OF JAPAN vol. 95, no. 1, 28 February 1995 & JP 06 278358 A (MITSUBISHI PAPER MILLS, LIMITED), 4 October 1994 * abstract *	1-9	TECHNICAL FIELDS SEARCHED (Int.C1.6) B41M
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Place of search THE HAGUE		Date of completion of the search 3 June 1999	Examiner Bacon, A
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ON EUROPEAN PATENT APPLICATION NO.**

EP 98 11 1534

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03-06-1999

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